

# **Testing and Refinement of Long Pathlength Liquid Core Waveguide Sensors for Autonomous In-Situ Analysis of the Upper Ocean**

Robert H. Byrne

College of Marine Science, University of South Florida

140 Seventh Avenue South, St. Petersburg, FL 33701

phone: (727) 553-1508 fax: (727) 553-1189 email: [byrne@marine.usf.edu](mailto:byrne@marine.usf.edu)

Eric Kaltenbacher

Center for Ocean Technology, University of South Florida

140 Seventh Avenue South, St. Petersburg, FL 33701

phone (727) 553-3959 fax: (727) 553-3967 email: [eak@marine.usf.edu](mailto:eak@marine.usf.edu)

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## **LONG -TERM GOALS**

This research project is directed toward the development of optoelectronic devices for measurement of key variables that influence oceanic biogeochemistry. The devices will have extraordinary sensitivity and versatility, and will be capable of rapid measurements in conjunction with adaptive sampling procedures, or long-term ocean measurements within large-scale ocean monitoring networks.

## **OBJECTIVES**

The broad objectives of this work are the testing, deployment and refinement of spectroscopic sensors for monitoring the distributions of reactive chemicals in seawater. The analytes of special interest in this work are iron, copper, nitrate, nitrite, ammonia, phosphate and CO<sub>2</sub>-system variables (total inorganic carbon, total alkalinity, CO<sub>2</sub> partial pressure and pH). The desired accuracy of the in-situ instrumentation is 0.1%, and the anticipated limit of detection for micronutrients is better than one nanomolar. The sensors should be capable of autonomous operations on a wide variety of platforms including AUVs, profiling floats, gliders and moorings.

## **APPROACH**

Due to both specificity and sensitivity, fluorometric and absorbance spectroscopy continue to be the instrumental methods of choice for laboratory and shipboard measurements of key biogeochemical variables. Since the concentrations of biologically essential nutrients in the upper ocean can be extremely low, conventional spectroscopic instrumentation is often incapable of resolving important relationships between ocean biology and ocean chemistry. Consequently, through the ONR funding on this project we have (a) pursued order of magnitude improvements in the sensitivity of conventional spectroscopic analysis for key oceanic nutrients and (b) undertaken the development of instrumentation which allows extremely sensitive and analyte-specific analyses to be performed in-situ. The salient benefits of this work include dramatic improvements in sensitivity, rates of sample analysis, and sample processing cleanliness. Furthermore data acquisition is near real-time, whereupon data acquisition and sampling strategy can be closely and interactively linked.

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The specific technological approach in this project involves the use of Teflon AF 2400 liquid core waveguides to achieve optical pathlengths as long as 10 meters in shipboard analyses (Lenes et al., 2001) and pathlengths between 30 cm and 5 meters for in-situ analyses. Through ONR support we pioneered the use of these waveguides for analysis of a wide variety of analytes in the laboratory: Fe, Cu, Cr, Mo,  $\text{HS}^-$ ,  $\text{NO}_2^-$ ,  $\text{NO}_3^-$ ,  $\text{NH}_3$ , total dissolved inorganic carbon and pH (Waterbury et al., 1997; Yao et al., 1998; Yao and Byrne, 1999; Byrne et al., 2000; Byrne et al., 2001). This work requires the refinement of conventional spectroscopic procedures that have detection limits on the order of 100 nanomolar to allow simple, robust measurements at nanomolar to subnanomolar concentration levels. Laboratory procedures are then further refined and adapted to in-situ spectroscopic instrumentation developed at the USF Center for Ocean Technology to provide robust in-situ chemical measurements (Steimle et al. 2002). As such this project entails chemical engineering, optoelectronic engineering, and scientific testing in both the laboratory and the field.

Current key personnel in this project include: R.H. Byrne (Lead Scientist), E.A. Kaltenbacher (Lead Engineer), E.T. Steimle (Chemical Engineer), Xuewu Liu (Marine Physical Chemist), Michael Callahan and Renate Bernstein (Chemical Oceanographers), Lori Adornato and Kelly Quinn (students).

## WORK COMPLETED

Four types of Spectrophotometric Elemental Analysis Systems (SEAS sensors) are currently being tested, developed and designed. The first of these, SEAS-I (Figure 1), is currently being tested in the laboratory and in the field. SEAS I has a two-pump mixing system, and is suitable for analyses in which a single reagent, or mixed reagent, is combined with a seawater sample-stream.

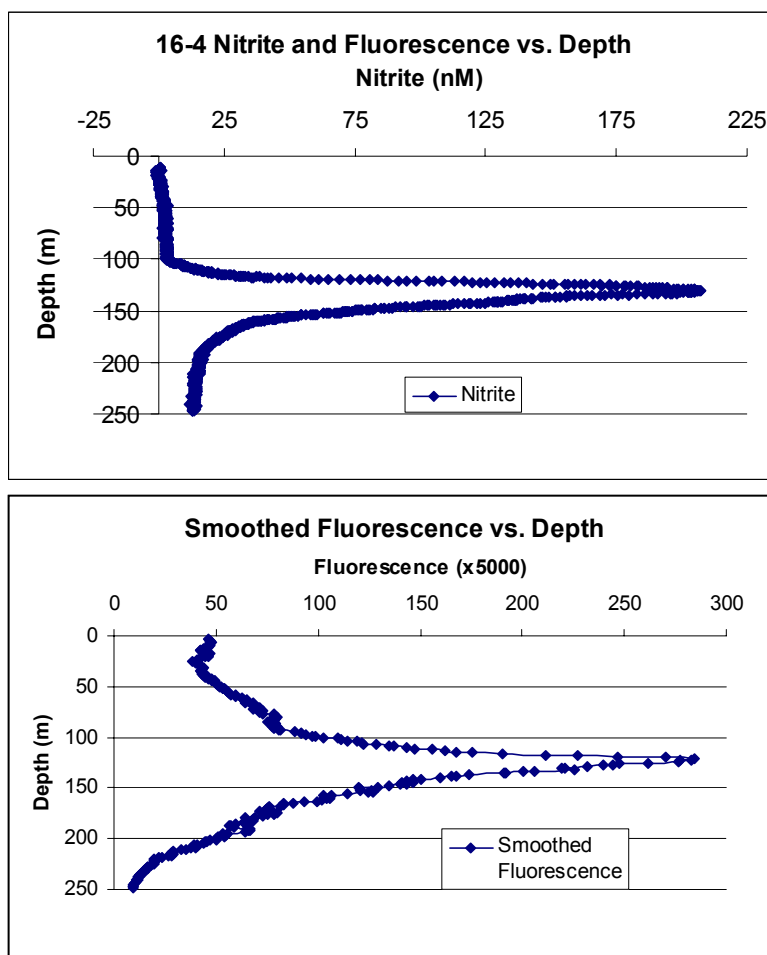


**Figure 1: The SEAS-I Sensor**

*[This picture of SEAS-I shows the system electronics and spectrophotometer housed in a transparent pressure housing (left) and the reagent/pumps/optical system (right) that is exposed to ambient seawater]*

SEAS-I is suitable for measurements of Fe(II), Fe(III), Cu,  $\text{NO}_2^-$ ,  $\text{NO}_3^-$ , pH and  $\text{pCO}_2$ . We have assembled a total of eight SEAS-I sensors for testing in the laboratory and in the field. Fe and Cu calibrations of SEAS-I in the laboratory show responses that are highly linear over a concentration range between several hundred nanomolar and less than one nanomolar. SEAS-I deployments for

measurements of Cu in Tampa Bay have shown that this highly bioactive element has strong horizontal gradients in local waters. SEAS-I was used for vertical nitrite profiling in the Pacific Ocean on a month-long cruise between Honolulu and San Diego. A nitrite profile typical of those obtained throughout the cruise is shown in Figure 2 along with comparative fluorescence measurements obtained at the same station. The SEAS-I instrument collected data every two seconds and provided unprecedented detail about the distribution on nitrite in the upper water column. This work shows that, using SEAS, the primary nitrite maximum (PNM) can be studied with high precision as it changes location and shape in response to varying diurnal distributions of microorganisms in the water column. Figure 2 shows that the PNM has a strikingly sharp profile in the water column.  $\text{NO}_2^-$  concentrations vary by a factor of approximately 100 over distances of 15 to 25 meters, whereby conventional sampling and shipboard analyses are likely to be problematic.



**Figure 2: A Nitrite versus Depth Profile in Oligotrophic Seawater Obtained with SEAS**  
*[This figure shows near zero nitrite concentrations between the surface and 110 meter depths, with concentrations sharply rising to a 210 nanomolar maximum at 130 meters. Concentrations at greater depth decline sharply and exhibit a shoulder at about 140 meters. The nitrite data, which were obtained every two seconds, exhibit a remarkably smooth profile that required no averaging. The fluorescence profile, shown for comparison with the  $\text{NO}_2^-$  profile, is remarkably similar in form and also with respect to the depth of its maximum. The fluorescence profile is far noisier than the  $\text{NO}_2^-$  profile and was processed using a moving average filter.]*

Laboratory calibrations of our SEAS-I system for pH analyses are now complete. The stability of our pH measurement system was greatly improved using a stronger light source and spectral shaping of transmitted light to allow stable measurements at the three wavelengths required for pH measurements. Since the sampling rates for  $\text{NO}_2^-$  and pH are quite similar, our results indicate that detailed measurements of covariations in nutrients and  $\text{CO}_2$ -system parameters are feasible using SEAS.

A second type of SEAS system (SEAS-II) is being designed to allow greater flexibility in chemical measurements. SEAS-II is essentially identical to SEAS-I, with a third reagent pump added to allow new types of measurements and/or refinements in the analyses that can be conducted via SEAS-I. SEAS-II sensors will be used for measurements of total dissolved inorganic carbon, ultra-trace levels of dissolved iron, and improved measurements of nitrate and copper.

A third type of SEAS system (SEAS-II-fluorescence) is under construction for fluorometric measurements of ammonia. Laboratory measurements show excellent linearity for concentrations up to 50 nanomolar, with a current detection limit on the order of 2 nanomolar. The sample processing rate at low ammonia concentrations is approximately 3 minutes per sample. Much higher rates are attainable at higher ambient ammonia concentrations.

Design and construction on a fourth type of SEAS sensor (SEAS-III) are complete, and initial sensor testing has begun. SEAS-III extends the depth capabilities of previous instruments (500 meters) to approximately 3000 meters, and allows multiple analyte measurements in a single instrument. Additional important innovations in SEAS-III are (a) the use of multiple syringe (piston) pumps for precise reagent delivery, and (b) use of a novel spectrometer design for improved measurement stability and accuracy. We anticipate that measurements with SEAS-III will be exceptionally robust.



***Figure 3: A SEAS-III Photograph.***

***[This Photograph shows the SEAS-III System Design. SEAS-III has an internal power supply, four piston-driven reagent pumps, and a system for combining reactive reagents immediately prior to analysis. This system considerably improves reagent longevity, and thereby extends measurement endurance.]***

## RESULTS

Two peer reviewed publications describing our ONR supported research were published in 2002 (Steimle et al., 2002; Byrne et al. 2002). The first of these works describes the first use of in-situ instrumentation to obtain chemical profiles at nanomolar concentration levels. The second work describes novel procedures that allow in-situ measurements of all directly measurable CO<sub>2</sub> system parameters. This ONR funded project has, to date, resulted in seven peer reviewed publications and two technical reports.

## IMPACT/APPLICATIONS

The SEAS sensors developed in this project can be used to markedly extend the limits of detection for a wide variety of influential chemicals in seawater, estuaries, rivers, lakes and subterranean waters. SEAS sensors provide real-time measurement capabilities, whereupon sampling strategies can be modified in response to observations. SEAS sensors are robust and, although relatively inexpensive, are orders of magnitude more sensitive than conventional spectrophotometers.

## TRANSITIONS

The Center for Ocean Technology is currently in discussions that should lead to commercial licensing of the SEAS-I sensor system. SEAS instruments are used as a teaching aid in the USF Oceanography Camp for middle-school-age girls each summer.

## RELATED PROJECTS

The SEAS-I instrument forms the basis for a NOAA project funded through the University of New Hampshire, “In-Situ Monitoring of a Reactive Metal in Riverine and Estuarine Mixing Zones”. SEAS-I sensors form the basis for the USF portion of a collaborative WHOI-USF proposal submitted to the National Science Foundation, “Collaborative Research: Continued Development and Sea Testing of Buoy-mounted Instruments: Time series Measurements of the Iron Concentrations in Dry and Wet Deposition to the Ocean”. SEAS instruments constitute the principal chemical sensors that are being used in the ONR funded project, “Bottom Stationed Ocean Profiler”. SEAS sensors form the basis for a newly funded collaborative ONR project with the University of Maine (Mary Jane Perry), “The role of Nutrients in the Formation, Maintenance and Transformation of Phytoplankton Thin Layers”.

## PUBLICATIONS

Steimle, E.T., Kaltenbacher, E.A., and Byrne, R.H. (2002), “In-Situ Nitrite Measurements Using a Compact Spectrophotometric Analysis System.”, *Marine Chemistry*, 77:255-261.

Byrne, R.H., Liu, X., Kaltenbacher, E., and Sell, K. (2002), “Spectrophotometric Measurement of Total Inorganic Carbon In Aqueous Solutions Using a Liquid Core Waveguide.”, *Analytica Chimica Acta*, 451: 221-229.

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